# EXHAUST GAS PURIFYING APPARATUS

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## Abstract

PROBLEM TO BE SOLVED: To provide an exhaust gas purifying apparatus by which particulate (PM) and nitrogen oxides (NOx) in an exhaust gas is removed at a high NOx removal rate while evading sulfur poisoning that is a weak point of NOx storage reduction type catalyst.
SOLUTION: In the exhaust gas purifying apparatus provided with a wall flow type filter 4 provided in an exhaust passage 3 of an engine 2 and for purifying the particulate in the exhaust gas G, an oxidation catalytic layer 20 supporting an oxidation catalyst 21 is provided on the upstream part of a porous wall surface 30 of the filter 4 and a nitrogen oxide purifying catalyst layer 40 supporting the nitrogen oxide storage reduction type catalyst 41 containing a nitrogen oxide storage material 41a and an oxidation catalyst 41b is provided on the downstream side part of the porous wall surface 30 of the filter 4.

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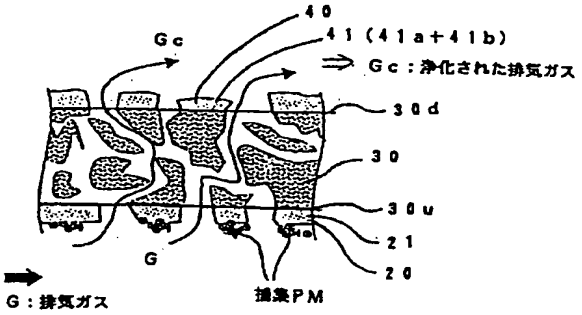
(54)【発明の名称】　排気ガス浄化装置

(57)【要約】
【課題】　ＮＯｘ吸蔵還元型触媒の弱点である硫黄被毒を回避しながら、高いＮＯｘ浄化率で、排気ガス中のＰＭとＮＯｘの浄化を行うことができる排気ガス浄化装置を提供する。
【解決手段】　エンジン２の排気通路３に設けられ、排気ガスＧ中の粒子状物質を浄化するウオールフロータイプのフィルタ４を備えた排気ガス浄化装置１において、前記フィルタ４の多孔質壁面３０の上流側部分に酸化触媒２１を担持した酸化触媒層２０を設けると共に、前記フィルタ４の多孔質壁面３０の下流側部分に窒素酸化物吸蔵物質４１ａと酸化触媒４１ｂを含む窒素酸化物吸蔵還元型触媒４１を担持した窒素酸化物浄化触媒層４０を設ける。



1

【特許請求の範囲】

【請求項１】　エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化するウオールフロータイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの多孔質壁面の上流側部分に酸化触媒を担持した酸化触媒層を設けると共に、前記フィルタの多孔質壁面の下流側部分に窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を設けたことを特徴とする排気ガス浄化装置。

【請求項２】　エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化する繊維積層タイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの上流側の繊維層に酸化触媒を担持させるか又は酸化触媒を担持した酸化触媒層を積層すると共に、前記フィルタの下流側の繊維層に、窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持させるか又は該窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を積層したことを特徴とする排気ガス浄化装置。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ディーゼルエンジン等の排気ガス中の粒子状物質及び窒素酸化物を、ディーゼルパティキュレートフィルタとこのフィルタに担持した窒素酸化物吸蔵還元型触媒で浄化する排気ガス浄化装置に関するものである。

【０００２】

【従来の技術】ディーゼルエンジンから排出される粒子状物質（ＰＭ：パティキュレート：以下ＰＭ）の排出量は、窒素酸化物（以下ＮＯｘ），一酸化炭素（以下ＣＯ）そして炭化水素（以下ＨＣ）等と共に年々規制が強化され、エンジンの改良のみでは、これらの規制に対応しきれなくなっており、これらの物質を排ガス後処理装置によって、低減する技術が開発されている。

【０００３】ＰＭの捕集に関しては、ディーゼルパティキュレートフィルタ（ＤＰＦ：Diesel Particulate Filter ：以下ＤＰＦ）があり、このＰＭを捕集するＤＰＦには多孔質のコーディエライトやセラミック製のモノリスハニカムのウオールフロータイプのフィルタや、セラミックや金属を繊維状にしてランダムに積層した繊維積層タイプのフィルタ等が研究開発され提案されている。

【０００４】このＰＭ捕集用のＤＰＦは、ＰＭの捕集に伴って目詰まりが進行し、捕集したＰＭの量の増加に伴って排気ガス圧力（排圧）が上昇するので、捕集したＰＭを除去する必要があるが、最近では、ＰＭの酸化除去を促進する酸化触媒をウオールフロータイプのフィルタの壁表面上に塗布した触媒付きフィルタで、ＰＭの捕集と捕集したＰＭの酸化除去を連続的に行う連続再生型ディーゼルパティキュレートフィルタが提案されている。

【０００５】このフィルタに担持させる酸化触媒には、排気ガス中の一酸化窒素（ＮＯ）を酸化して二酸化窒素

2

（$NO_2$）にする触媒や、ＰＭを低温から直接酸素（$O_2$）で酸化させるＰＭ酸化触媒（貴金属酸化触媒や酸化物酸化触媒）等がある。

【０００６】一方、ＮＯｘの浄化に関しては、その一つの手段としてＮＯｘ還元触媒があり、特開２０００－２８２８５２号公報では、ウオールフロータイプのフィルタの壁面のエンジン側にＮＯｘ還元触媒層と酸化触媒層を被覆した排気浄化装置と、ウオールフロータイプのフィルタの壁面のエンジン側に酸化触媒を、排気出口側にＮＯｘ還元触媒層をそれぞれ被覆した排気浄化装置が提案されている。

【０００７】これらの排気浄化装置では、フィルタと貴金属系触媒等の酸化触媒層とゼオライト系触媒等のＮＯｘ還元触媒層を一体化して装置を小型軽量化すると共に、酸化触媒層とＮＯｘ還元触媒層の配置の工夫により、酸化触媒でＰＭの燃焼の促進して、ＮＯｘ還元触媒へのＰＭ付着によるＮＯｘ還元効率の低下を回避し、また、フィルタ再生時のＰＭ燃焼時のＮＯｘ還元触媒への熱影響を少なくしてＮＯｘ還元触媒の劣化を防止している。

【０００８】

【発明が解決しようとする課題】しかしながら、特開２０００－２８２８５２号公報で提案されている、これらの排気浄化装置においては、ＮＯｘ浄化に、ＮＯｘ還元触媒を使用しているので、ＮＯｘ還元のために常時炭化水素等の還元剤を供給する必要があり、この還元剤を供給するための還元剤供給装置が必要となる。

【０００９】そして、この還元剤にエンジンの燃料を流用した場合には、燃料を排気通路に噴射するための噴射弁や配管が必要になる上に、燃費の悪化を招くという問題があり、また、エンジンの燃料以外のアンモニアや尿素を使用する場合には、噴射弁や配管に加えて、これらの還元剤用のタンクが必要になる上に、これらの還元剤を還元剤用のタンクに適宜補給する必要があるという問題がある。

【００１０】この排気通路への還元剤供給システムの設置が必要になると、特に既存の車両に、排気ガス装置を取り付ける際の作業が面倒になるので、装置面からも作業工数の面からコストアップとなり実用化が難しくなるという問題が発生する。

【００１１】また、特に、還元剤を必要とするＮＯｘ還元触媒の上流側に酸化触媒が配置されているため、還元剤が軽油の場合には酸化触媒により分解されてＮＯｘ還元効率のよい低分子量の炭化水素になり、また、ＳＯＦ（可溶性有機成分）も分解されて還元剤として、効率よくＮＯｘを還元するとされているが、ディーゼルエンジンの通常の燃焼状態のように排気中の酸素濃度が高い場合には、排気通路内に供給された還元剤は、上流側の酸化触媒によって酸化される可能性が大きく、ＮＯｘ還元効率も低下し、燃費の悪化を招くと考えられる。

【００１２】一方、排気ガス中のＮＯｘを除去するための触媒の一つに、ＮＯｘ吸蔵還元型触媒がある。このＮＯｘ吸蔵還元型触媒は、ＮＯｘ吸蔵機能を持つバリウム等のＮＯｘ吸蔵物質と酸化触媒機能を有する白金等の活性触媒金属（酸化触媒）とを担持して、排気ガス中の酸素濃度等によってＮＯｘ吸蔵とＮＯｘ放出及び還元浄化の機能を果たす触媒である。

【００１３】本発明は、上述の問題を解決するためになされたものであり、その目的は、ＤＰＦのフィルタの上流側部分に酸化触媒を、また、下流側部分にＮＯｘ吸蔵還元型触媒をそれぞれ配備し、ＮＯｘ吸蔵還元型触媒の弱点である硫黄被毒を回避しながら、高いＮＯｘ浄化率で、排気ガス中のＰＭとＮＯｘの浄化を行うことができる排気ガス浄化装置を提供することにある。

【００１４】

【課題を解決するための手段】以上のような目的を達成するための排気ガス浄化装置は、次のように構成される。

【００１５】１）エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化するウオールフロータイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの多孔質壁面の上流側部分に酸化触媒を担持した酸化触媒層を設けると共に、前記フィルタの多孔質壁面の下流側部分に窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を設けて構成される。

【００１６】このウオールフロータイプのフィルタは、多孔質のセラミックのハニカムのチャンネルの入口と出口を交互に目封じしたモノリスハニカム等で形成でき、酸化触媒を担持した酸化触媒層は、このフィルタの多孔質壁面に塗布されたゼオライトやアルミナ等の多孔質触媒コート層に、白金（Ｐｔ）や酸化セリウム（$CeO_2$）等の酸化触媒を担持する等して形成できる。

【００１７】また、窒素酸化物（ＮＯｘ）吸蔵還元型触媒は、排気ガス中の$O_2$濃度やＣＯ濃度によってＮＯｘ吸蔵とＮＯｘ放出及び還元・浄化の機能を持つものであり、ＮＯｘ吸蔵機能を持つカリウム（Ｋ）、バリウム（Ｂａ）、ランタン（Ｌａ）等のＮＯｘ吸蔵物質と、白金（Ｐｔ）やロジウム（Ｒｈ）等の触媒活性金属からなる酸化触媒とで形成でき、ＮＯｘ浄化触媒層は、フィルタの多孔質壁面に塗布されたゼオライトやアルミナ等の多孔質触媒コート層に、これらのＮＯｘ吸蔵物質と酸化触媒を担持する等して形成できる。

【００１８】２）または、エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化する繊維積層タイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの上流側の繊維層に酸化触媒を担持させるか又は酸化触媒を担持した酸化触媒層を積層すると共に、前記フィルタの下流側の繊維層に、窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持させるか又は該窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を積層して構成される。

【００１９】この繊維積層タイプのフィルタには、アルミナ等のセラミックの繊維や金属繊維をランダムに積層した不織布の繊維層を一層乃至数層重ねて形成し、この繊維層の積層体を耐熱金網で挟持し蛇腹状に折り曲げて中空円筒状に構成して、外側から内側へ排気ガスを流通させることにより、排気ガスを浄化するフィルタ等がある。

【００２０】この上流側又は下流側の繊維層をそれぞれの触媒の溶液に浸せきして、繊維層を形成する繊維表面にそれぞれの触媒を担持させて形成する。又は、繊維積層タイプのフィルタの繊維層の積層体の上流側の繊維層の表面に酸化触媒を担持した多孔質触媒コート層を塗布し、また、下流側の繊維層の表面に上記と同様なＮＯｘ吸蔵還元型触媒を担持した多孔質触媒コート層を塗布する。

【００２１】これらの構成により、フィルタの上流側部分に酸化触媒を、また、下流側にＮＯｘ吸蔵還元型触媒をそれぞれ担持させることにより、上流側の酸化触媒で排気ガス中の硫黄酸化物（ＳＯｘ）を酸化し、排気ガス中のＣａ，Ｚｎ，Ｆｅ等と化合させて、固体のサルフェートにして、フィルタに捕集させるので、ＳＯｘのＮＯｘ吸蔵還元型触媒への到達を防止でき、ＮＯｘ吸蔵還元型触媒の硫黄被毒を回避できる。

【００２２】そして、ＮＯｘ吸蔵還元型触媒は、一酸化炭素（ＣＯ）が存在すると、ＮＯｘ吸蔵物質から二酸化窒素（$NO_2$）を放出する特性を持っているために、空燃比がリーンのＮＯｘ吸蔵運転の時に、排ガス中にＣＯが存在すると、ＮＯｘ吸蔵能力が低下してしまうが、本発明の排気ガス浄化装置では、上流側の酸化触媒で排気ガス中のＣＯを酸化して除去するので、空燃比がリーン時におけるＮＯｘ吸蔵能力を高く維持できる。

【００２３】また、空燃比がリッチの再生運転の時には、排気ガス中に酸素（$O_2$）が無いために、大量のＣＯが発生するので、このＣＯがＮＯｘ吸蔵物質からの$NO_2$の放出を促進すると共に、このＣＯは還元剤となるので、放出された$NO_2$はＮＯｘ吸蔵還元型触媒の酸化触媒により効率よく還元浄化される。

【００２４】

【発明の実施の形態】以下、本発明に係る実施の形態の排気ガス浄化装置について、図面を参照しながら説明する。

【００２５】図１に、この第１の実施の形態の排気ガス浄化装置１の構成を示す。

【００２６】この排気ガス浄化装置１は、図１に示すように、ディーゼルエンジン２の排気通路３に設けられる装置であり、排気ガスＧ中の粒子状物質（ＰＭ）と窒素酸化物（ＮＯｘ）を浄化するウオールフロータイプのフィルタ４を備えて構成される。

【００２７】図２に示すように、このウオールフロータイプのフィルタ４は、コーディエライト、炭化ケイ素（ＳｉＣ）やステンレス等で形成される構造材の担持体３０に、排気ガスＧの通路となる多数の多角形形状のチャンネル（セル）３５を有しており、多孔質のセラミックのハニカムのチャンネル３５の入口と出口を交互に目封じしたモノリスハニカム等で形成される。

【００２８】そして、図３及び図４に示すように、このフィルタ４の多孔質壁面３０の上流側部分３０ｕに、酸化触媒２１を担持した通気可能な酸化触媒層２０を設けると共に、フィルタ４の多孔質壁面３０の下流側部分３０ｄに、窒素酸化物吸蔵物質（ＮＯｘ吸蔵物質）４１ａと酸化触媒４１ｂを含む窒素酸化物吸蔵還元型触媒（ＮＯｘ吸蔵還元型触媒）４１を担持した通気可能なＮＯｘ浄化触媒層４０を設ける。

【００２９】この酸化触媒層２０は、このフィルタ４の多孔質壁面３０の上流側部分３０ｕに塗布されたゼオライトやアルミナ（$Al_2O_3$）等の多孔質触媒コート層に、白金（Ｐｔ）等や酸化セリウム（$CeO_2$）等の酸化触２１を担持して通気可能に形成される。

【００３０】また、ＮＯｘ浄化触媒層４０は、フィルタ２の多孔質壁面３０の下流側部分３０ｄに塗布されたゼオライトやアルミナ等の多孔質触媒コート層に、ＮＯｘ吸蔵物質４１ａと酸化触媒４１ｂとからなるＮＯｘ吸蔵還元型触媒４１を担持して形成される。

【００３１】このＮＯｘ吸蔵物質４１ａはＮＯｘ吸蔵機能を持つカリウム（Ｋ）、バリウム（Ｂａ）、ナトリウム（Ｎａ）、リチウム（Ｌｉ）、セシウム（Ｃｓ）等のアルカリ金属や、カルシウム（Ｃａ）等のアルカリ土類、ランタン（Ｌａ）、イットリウム（Ｙ）等の希土類等の中の一つ又は幾つかの組み合わせで形成され、酸化触媒４１ｂは白金（Ｐｔ）やロジウム（Ｒｈ）等の触媒活性金属で形成される。

【００３２】この構成により、ＮＯｘ吸蔵還元型触媒４１は、図９に模式的に示すように、排気ガス中の空燃比がリーン状態（$O_2$濃度が比較的高い）の時にＮＯｘ吸蔵物質４１ｂでＮＯｘを吸蔵し、空燃比がリッチ状態（$O_2$濃度が殆どゼロ）の時にＮＯｘ吸蔵物質４１ｂでＮＯｘを放出し、この放出したＮＯｘを、酸化触媒４１ｂの触媒作用によりＣＯやＨＣ等の還元剤で還元して浄化する機能を持つことになる。

【００３３】次に、第２の実施の形態の排気ガス浄化装置１Ａについて説明する。

【００３４】この第２の実施の形態の排気ガス浄化装置１Ａは、図５～図７に示すように、第１の実施の形態の排気ガス浄化装置１と排気ガス中の粒子状物質（ＰＭ）を浄化するフィルタのタイプが異なる。

【００３５】この第２の実施の形態のフィルタ４Ａ，４Ｂ，４Ｃは、図５～図１０に示すように、繊維積層タイプのフィルタで形成され、アルミナ等のセラミックの繊維や金属繊維をランダムに積層した不織布の繊維層５ａ～５ｄを一層乃至数層重ねて形成し、この繊維層５ａ～５ｄの積層体５Ａ，５Ｂ，５Ｃを耐熱金網６、７で挟持し蛇腹状に折り曲げて中空円筒状に構成し、この中空円筒の一端側４ａを閉塞する。排気ガスＧは、この中空円筒状の繊維層５ａ～５ｄの積層体５Ａ，５Ｂ，５Ｃの外側から内側へ流通し浄化され、中空部４ｂの他端側４ｃから外部へ排出される。

【００３６】そして、図８及び図９に示すように、このフィルタ４Ａ，４Ｂの上流側の繊維層５ａの表面に、酸化触媒２１を担持した多孔質触媒コート層２０を塗布し、また、下流側の繊維層５ｄの表面にＮＯｘ吸蔵還元型触媒４１を担持した多孔質触媒コート層４０を塗布する。図８は、繊維層５ａの耐熱金網６側、及び繊維層５ｄの耐熱金網７側に、多孔質触媒コート層２０、４０を設けた積層体５Ａの例を示し、図９は、繊維層５ａと繊維層５ｂとの間、及び繊維層５ｄと繊維層５ｃとの間に、多孔質触媒コート層２０、４０を設けた積層体５Ｂの例を示す。

【００３７】若しくは、上流側又は下流側の繊維層５ａ，５ｄをそれぞれの触媒３１，４１の溶液に浸せきした後乾燥及び熱処理して繊維層５ａ，５ｄを形成する繊維表面にそれぞれの触媒３１，４１を担持させてから、図１０に示すように、この触媒３１，４１を担持した繊維層５ａ’，５ｄ’を、触媒を担持していない繊維層５ｂ，５ｃに積層して、積層体５Ｃを形成する。なお、フィルタ４Ｃを構成する繊維層５ａ～５ｄ全部にいずれかの触媒を担持させて、触媒を担持していない繊維層を省いて形成してもよい。

【００３８】以上の構成の排気ガス浄化装置１、１Ａによれば、排気ガスＧは酸化触媒２１に接触し他後に、フィルタ４，４Ａ～４Ｃを通過して、更に、ＮＯｘ吸蔵還元型触媒４１に接触してから排出されるので、次のようなプロセスで効率よく浄化される。

【００３９】先ず、通常のディーゼルエンジンや希薄燃焼ガソリンエンジン等の通常運転のように、排気ガス中に$O_2$が含まれる空燃比がリーンの酸素濃度が比較的高い状態では、図１１に示すように、フィルタ４，４Ａ～４Ｃの上流側の酸化触媒２１や下流側のＮＯｘ吸蔵還元型触媒の酸化触媒４１ｂで、排気ガスＧ中のＮＯは、この排気ガスＧ中の$O_2$により酸化されて$NO_2$になり、この$NO_2$は、バリウム（Ｂａ）等のＮＯｘ吸蔵物質４１ａが硝酸塩（例えば$Ba(NO_3)_2$）等の形で吸蔵するので、排気ガスＧ中のＮＯｘが浄化される。

【００４０】また、上流側の酸化触媒２１で、排気ガスＧ中のＨＣ，ＣＯを酸化浄化し、ＮＯｘ吸蔵還元型触媒４１のＣＯによるＮＯｘ吸蔵能力の劣化を防止する。また、ＳＯＯＴ（スート：煤）等のＰＭはフィルタ４，４Ａ～４Ｃの多孔質壁面３０や繊維の積層体５Ａ～５Ｃで捕集される。

【００４１】しかし、この状態が継続すると、ＮＯｘ吸蔵機能を持つＮＯｘ吸蔵物質４１ａは、全て硝酸塩等に変化してＮＯｘ吸蔵機能を失ってしまうので、エンジンの運転状態を変更して、理論空燃比及び理論空燃比に近い空燃比であるリッチ燃焼を短時間（例えば、約０．１秒～５秒程度）の間だけ行って、リッチスパイクガスと呼ばれる、排気ガス中の$O_2$を略ゼロとした高温の排気ガスを発生させて、ＮＯｘ吸蔵還元型触媒４１に送り、再生処理する。

【００４２】そして、ＮＯｘ吸蔵還元型触媒４１を再生する空燃比がリッチの酸素濃度は殆どゼロの状態では、フィルタ４，４Ａ～４Ｃの上流側では、$O_2$が殆どないため、ＨＣ，ＣＯは酸化されることなく、下流側に通過し、下流側では$O_2$が殆どないので、図１２に示すように、ＮＯｘを吸蔵したＮＯｘ吸蔵物質４１ａの硝酸塩（硝酸バリウム）等は元の状態（バリウム）に戻り、吸蔵していた$NO_2$を放出する。

【００４３】この再生時には、ＣＯが多いため、ＮＯｘ吸蔵物質４１ａからの$NO_2$の放出と還元浄化を促進させることができるので、ＮＯｘ吸蔵能力の再生に要する時間を短縮できる。

【００４４】この放出された$NO_2$は、排気ガス中に$O_2$が存在しないので、酸化触媒４１ｂの触媒作用により多孔質壁面３０や繊維の積層体５Ａ～５Ｃを通過してきた排気ガス中のＣＯ，ＨＣ，$H_2$等を還元剤として、窒素$N_2$に還元され浄化され、$H_2O$，$CO_2$と共に排出される。また、ＳＯＯＴ等のＰＭは多孔質壁面３０や繊維の積層体５Ａ～５Ｃで捕集される。

【００４５】そして、排気ガス中の硫黄酸化物（ＳＯｘ）を上流側の酸化触媒３１で酸化して、排気ガス中のＣａ，Ｚｎ，Ｆｅ等と化合させて、固体のサルフェートにすることができ、このサルフェートは多孔質壁面３０や繊維の積層体５Ａ～５Ｃで捕集できるので、ＳＯｘのＮＯｘ吸蔵還元型触媒４１への接触を防止して、ＮＯｘ吸蔵還元型触媒４１の硫黄被毒を回避できる。

【００４６】

【発明の効果】以上に説明したように、本発明の排気ガス浄化装置によれば、次のような効果を奏することができる。

【００４７】常時ＮＯｘ還元用の還元剤を供給することなく、酸化触媒とＮＯｘ吸蔵還元型触媒を担持したフィルタにより、排気ガス中のＰＭを捕集及び酸化して浄化できると共に、排気ガス中のＮＯｘをＮＯｘ吸蔵還元型触媒による吸蔵、及び放出と還元により、効率よく浄化することができるので、還元剤供給装置が不要になり、燃費の悪化を防止できる。

【００４８】そして、フィルタの上流側部分に酸化触媒を、また、下流側部分にＮＯｘ吸蔵還元型触媒を配設する構成により、上流側部分の酸化触媒で排気ガス中の硫黄酸化物（ＳＯｘ）を酸化して、排気ガス中のＣａ，Ｚｎ，Ｆｅ等と化合させて、フィルタで捕集できる固体のサルフェートとし、フィルタで捕集するので、排気ガス中のＳＯｘがＮＯｘ吸蔵還元型触媒への到達するのを防止でき、ＮＯｘ吸蔵還元型触媒の硫黄被毒を回避できる。

【００４９】更に、空燃比がリーンのＮＯｘ吸蔵運転において、フィルタの上流側の酸化触媒で排気ガス中のＣＯを酸化除去するので、ＣＯによるＮＯｘ吸蔵能力の劣化を防止して高い浄化率を維持でき、また、空燃比がリッチの再生運転において、排気ガス中に$O_2$が無いために発生するＣＯで、ＮＯｘ吸蔵物質からの$NO_2$の放出と還元浄化を促進させることができ、ＮＯｘ吸蔵能力の再生に要する時間を短縮できる。

【図面の簡単な説明】

【図１】本発明に係る排気ガス浄化装置の配置を示す図である。

【図２】本発明に係る第１の実施の形態の排気ガス浄化装置のウオールフロータイプのフィルタの構成を示す図である。

【図３】図２のフィルタの拡大図である。

【図４】図２のフィルタの部分拡大図である。

【図５】本発明に係る第２の実施の形態の排気ガス浄化装置の繊維積層タイプのフィルタの構成を示す図である。

【図６】図５のフィルタにおける排気ガスの流れを示す図である。

【図７】図６の部分拡大図である。

【図８】図５のフィルタの積層構造の第１例を示す図である。

【図９】図５のフィルタの積層構造の第２例を示す図である。

【図１０】図５のフィルタの積層構造の第３例を示す図である。

【図１１】ＮＯｘ吸蔵還元型触媒によるＮＯｘ浄化のメカニズムを示す模式的な図で、通常燃焼等の空燃比がリーン状態の排気ガスを供給している状態を示す。

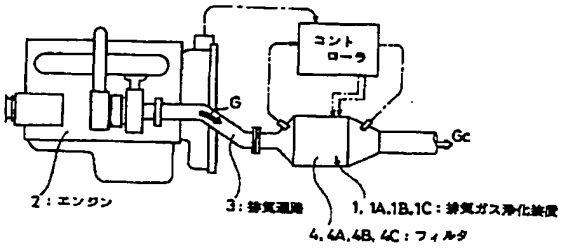
【図１２】ＮＯｘ吸蔵還元型触媒によるＮＯｘ排気浄化のメカニズムを示す模式的な図で、空燃比がリッチ状態の排気ガスを供給している状態を示す。

【符号の説明】

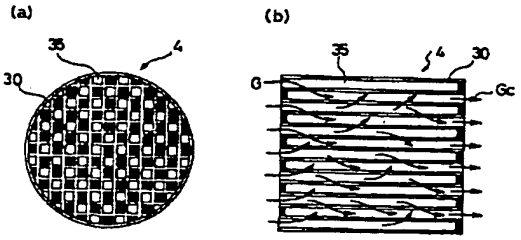
１，１Ａ，１Ｂ，１Ｃ　排気ガス浄化装置
２　エンジン
３　排気通路
４　ウオールフロータイプのフィルタ
４Ａ，４Ｂ，４Ｃ　繊維積層タイプのフィルタ
４ａ　上流側の繊維層
４ｄ　下流側の繊維層
２０　酸化触媒層（多孔質触媒コート層）
２１　酸化触媒
３０　多孔質壁面

４０　窒素酸化物浄化触媒層（多孔質触媒コート層）
４１　窒素酸化物吸蔵還元型触媒（ＮＯｘ吸蔵還元型触媒）
＊４１ａ　窒素酸化物吸蔵物質（ＮＯｘ吸蔵物質）
４１ｂ　酸化触媒
＊　Ｇ　排気ガス

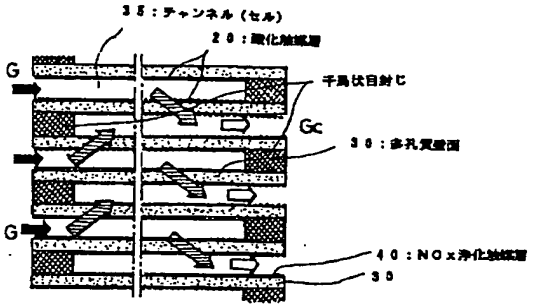
【図１】



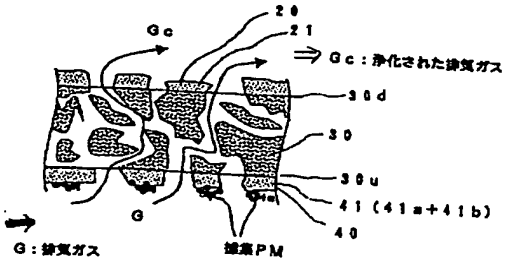

【図２】



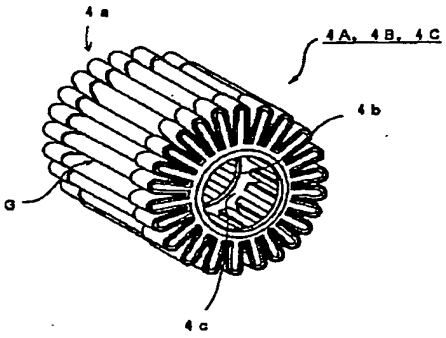

【図３】



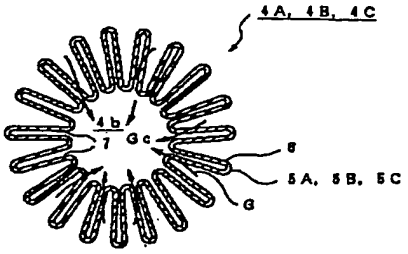

【図４】



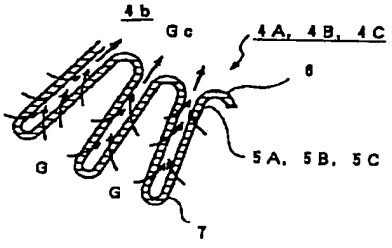

【図５】



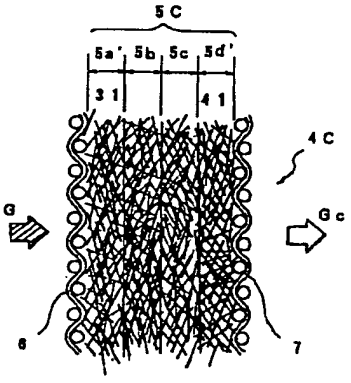

【図６】



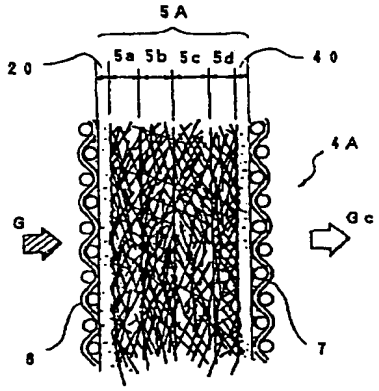

【図７】



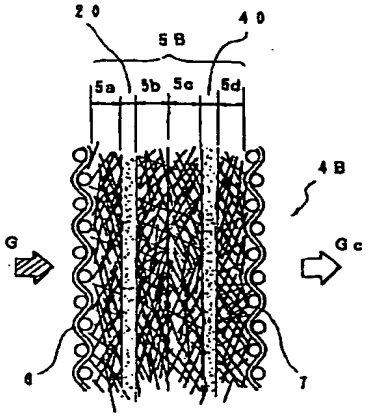

【図１０】



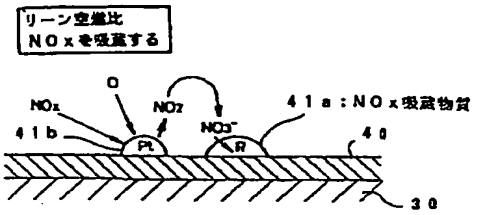
【図８】



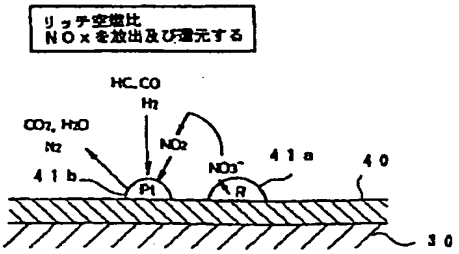

【図９】




【図１１】




【図１２】

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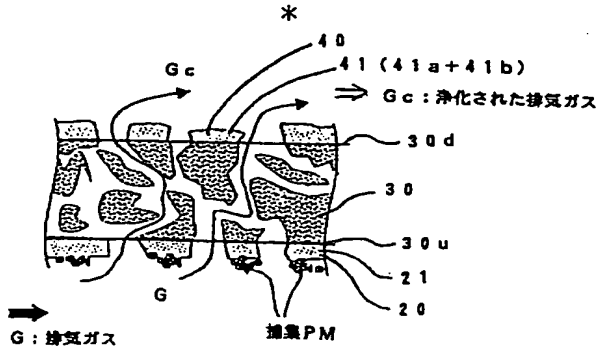
【手続補正書】
【提出日】平成１３年８月８日（２００１．８．８）
【手続補正１】
【補正対象書類名】図面
【補正対象項目名】図４

＊【補正方法】変更
【補正内容】
【図４】

＊



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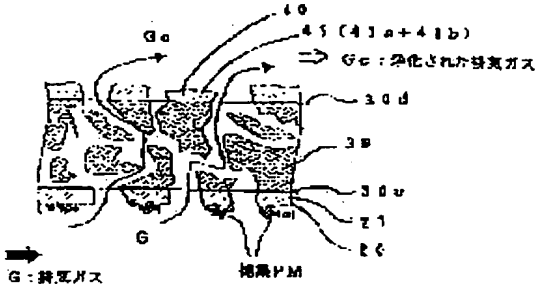
## (54) EXHAUST GAS PURIFYING APPARATUS

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an exhaust gas purifying apparatus by which particulate (PM) and nitrogen oxides (NOx) in an exhaust gas is removed at a high NOx removal rate while evading sulfur poisoning that is a weak point of NOx storage reduction type catalyst.
SOLUTION: In the exhaust gas purifying apparatus provided with a wall flow type filter 4 provided in an exhaust passage 3 of an engine 2 and for purifying the particulate in the exhaust gas G, an oxidation catalytic layer 20 supporting an oxidation catalyst 21 is provided on the upstream part of a porous wall surface 30 of the filter 4 and a nitrogen oxide purifying catalyst layer 40 supporting the nitrogen oxide storage reduction type catalyst 41 containing a nitrogen oxide storage material 41a and an oxidation catalyst 41b is provided on the downstream side part of the porous wall surface 30 of the filter 4.



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## CLAIMS

[Claim(s)]
[Claim 1] The exhaust gas purge characterized by preparing the nitrogen-oxides purification catalyst bed which supported the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occulded substance and an oxidation catalyst in the downstream part of the porosity wall surface of said filter while being prepared in the engine flueway and preparing the oxidation catalyst layer which supported the oxidation catalyst into the upstream part of the porosity wall surface of said filter in the exhaust gas purge equipped with the filter of the Wall flow type which purifies the particulate matter in exhaust gas.
[Claim 2] In the exhaust gas purge equipped with the filter of the fiber laminating type which is formed in an engine flueway and purifies the particulate matter in exhaust gas While carrying out the laminating of the oxidation catalyst layer which the fiber layer of the upstream of said filter was made to support an oxidation catalyst, or supported the oxidation catalyst The exhaust gas purge characterized by carrying out the laminating of the nitrogen-oxides purification catalyst bed which was made to support the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occulded substance and an oxidation catalyst in the fiber layer of the downstream of said filter, or supported this nitrogen-oxides occlusion reduction type catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the exhaust gas purge which purifies the particulate matter and nitrogen oxides in exhaust gas, such as a diesel power plant, with the nitrogen-oxides occlusion reduction type catalyst supported in a diesel particulate filter and this filter.
[0002]
[Description of the Prior Art] The technique of regulation being tightened up every year with nitrogen oxides (henceforth, NOx), a carbon monoxide (henceforth, CO), a hydrocarbon (henceforth, HC), etc., and it being impossible for the discharge of the particulate matter (PM: particulate : henceforth, PM) discharged from a diesel power plant to be unable to respond to these regulations only by engine amelioration, and reducing these matter with exhaust gas after-treatment equipment is developed.
[0003] About the uptake of PM, there is a diesel particulate filter (DPF:Diesel Particulate Filter : henceforth, DPF), and the Wall flow type filter of the monolith honeycomb of porous cordierite or the product made from a ceramic, the filter of the fiber laminating type which made the ceramic metallurgy group fibrous and carried out the laminating at random, etc. are done [ research and development in them etc. ] and proposed by DPF which carries out uptake of this PM.
[0004] Blinding advances in connection with the uptake of PM, and although DPF for these PM uptake needs to remove PM which carried out uptake since the exhaust-air-pressure force (exhaust gas pressure) goes up with the increment in the amount of PM which carried out uptake Recently, the continuation playback mold diesel particulate filter which performs continuously oxidation removal of PM which carried out uptake to the uptake of PM is proposed with the filter with a catalyst which applied the oxidation catalyst which promotes oxidation removal of PM on the wall front face of a Wall flow type filter.
[0005] There are a catalyst which oxidizes and uses the nitrogen monoxide in exhaust gas (NO) as a nitrogen dioxide (NO2), a PM oxidation catalyst (a noble-metals oxidation catalyst and oxide oxidation catalyst) which oxidizes PM with direct oxygen (O2) from low temperature as oxidation catalyst which this filter is made to support.
[0006] On the other hand, about purification of NOx, there is an NOx reduction catalyst as the one means, and the exhaust emission control device which covered the NOx reduction catalyst layer, respectively is proposed by the exhaust air outlet side in the oxidation catalyst by JP,2000-282852,A at the engine side of the wall surface of the exhaust emission control device which covered the NOx reduction catalyst layer and the oxidation catalyst layer to the engine side of the wall surface of a Wall flow type filter, and a Wall flow type filter.
[0007] While unifying a filter, oxidation catalyst layers, such as a noble-metals system catalyst, and NOx reduction catalyst layers, such as a zeolitic catalyst, and forming equipment into small lightweight in these exhaust emission control devices By the device of arrangement of an oxidation catalyst layer and an NOx reduction catalyst layer, combustion of PM promotes by the oxidation catalyst. Decline in the NOx reduction effectiveness by PM adhesion in an NOx reduction catalyst was avoided, and the thermal effect to the NOx reduction catalyst at the time





of PM combustion at the time of filter playback was lessened, and degradation of an NOx reduction catalyst is prevented.
[0008]
[Problem(s) to be Solved by the Invention] However, in these exhaust emission control devices proposed by JP,2000-282852,A, since the NOx reduction catalyst is used for NOx purification, it is necessary to always supply reducing agents, such as a hydrocarbon, for NOx reduction, and the reducing-agent feeder for supplying this reducing agent is needed.
[0009] and when an engine fuel is diverted to this reducing agent In the injection valve and piping for injecting a fuel to a flueway are needed upwards, and there is a problem of causing aggravation of fuel consumption and using ammonia and the ureas other than an engine fuel There is a problem that in addition to an injection valve or piping the tank for these reducing agents is needed upwards, and it is necessary to supply these reducing agents to the tank for reducing agents suitably.
[0010] If installation of the reducing-agent distribution system to this flueway is needed, since the activity at the time of attaching exhaust gas equipment in the existing car will become troublesome especially, the problem that become the field of an activity man day to a cost rise also from an equipment side, and utilization becomes difficult occurs.
[0011] Moreover, since the oxidation catalyst is arranged at the upstream of the NOx reduction catalyst which needs a reducing agent especially, When a reducing agent is gas oil, although it is decomposed by the oxidation catalyst, and it becomes the hydrocarbon of low molecular weight with sufficient NOx reduction effectiveness, and SOF (fusibility organic component) is also decomposed and NOx is efficiently returned as a reducing agent Like the usual combustion condition of a diesel power plant, when the oxygen density under exhaust air is high, possibility that the reducing agent supplied in the flueway will oxidize according to the oxidation catalyst of the upstream is large, and NOx reduction effectiveness also falls and is considered to cause aggravation of fuel consumption.
[0012] On the other hand, an NOx occlusion reduction type catalyst is in one of the catalysts for removing NOx in exhaust gas. This NOx occlusion reduction type catalyst is a catalyst which supports NOx occulded substarices, such as barium with an NOx occlusion function, and activity catalyst metals (oxidation catalyst), such as platinum which has an oxidation catalyst function, and achieves the function of NOx occlusion, NOx emission, and reduction purification by the oxygen density in exhaust gas etc.
[0013] Made in order that this invention may solve an above-mentioned problem, arranging an oxidation catalyst into the upstream part of the filter of DPF, and it arranging an NOx occlusion reduction type catalyst into a downstream part, respectively, and avoiding sulfur poisoning which is the weak spot of an NOx occlusion reduction type catalyst, the purpose is a high rate of NOx purification, and is to offer the exhaust gas purge which can purify PM and NOx in exhaust gas.
[0014]
[Means for Solving the Problem] The exhaust gas purge for attaining the above purposes is constituted as follows.
[0015] 1) While being prepared in an engine flueway and preparing the oxidation catalyst layer which supported the oxidation catalyst into the upstream part of the porosity wall surface of said filter in the exhaust gas purge equipped with the filter of the Wall flow type which purifies the particulate matter in exhaust gas, the nitrogen-oxides purification catalyst bed which supported the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occulded substance and an oxidation catalyst in the downstream part of the porosity wall surface of said filter is prepared, and it is constituted.
[0016] This Wall flow type of filter can be formed by the monolith honeycomb which ******(ed) the porous inlet port and porous outlet of a channel of a ceramic by turns, and the oxidation catalyst layer which supported the oxidation catalyst can be formed in porous catalyst coat layers applied to the porosity wall surface of this filter, such as a zeolite and an alumina, by carrying out supporting the oxidation catalyst of platinum (Pt), cerium oxide (CeO2), etc. [ of a honeycomb ]
[0017] Moreover, a nitrogen-oxides (NOx) occlusion reduction type catalyst O2 in exhaust gas





NOx occulded substances, such as a potassium (K) which has the function of NOx occlusion, NOx emission, and reduction and purification, and has an NOx occlusion function with concentration or CO concentration, barium (Ba), and a lanthanum (La), It can form by the oxidation catalyst which consists of catalytic activity metals, such as platinum (Pt) and a rhodium (Rh), and an NOx purification catalyst bed can be formed in porous catalyst coat layers applied to the porosity wall surface of a filter, such as a zeolite and an alumina, by carrying out supporting these NOx occulded substances and oxidation catalysts etc.
[0018] 2) Or it is prepared in an engine flueway and set to the exhaust gas purge equipped with the filter of the fiber laminating type which purifies the particulate matter in exhaust gas. While carrying out the laminating of the oxidation catalyst layer which the fiber layer of the upstream of said filter was made to support an oxidation catalyst, or supported the oxidation catalyst The laminating of the nitrogen-oxides purification catalyst bed which was made to support the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occulded substance and an oxidation catalyst in the fiber layer of the downstream of said filter, or supported this nitrogen-oxides occlusion reduction type catalyst is carried out, and it is constituted.
[0019] There is a filter which purifies exhaust gas among this fiber laminating type of the filters one layer thru/or by forming several layers in piles, pinching the layered product of this fiber layer at a heat-resistant wire gauze, bending in the shape of bellows, constituting in a bell shape, and circulating exhaust gas from an outside to the inside about the fiber layer of the nonwoven fabric which carried out the laminating of the fiber metallurgy group fiber of ceramics, such as an alumina, at random.
[0020] The dipping of the fiber layer of a besides style side or the downstream is carried out to the solution of each catalyst, and the fiber front face which forms a fiber layer is made to support each catalyst, and it forms in it. Or the porous catalyst coat layer which applied to the front face of the fiber layer of the upstream of the layered product of the fiber layer of a fiber laminating type filter the porous catalyst coat layer which supported the oxidation catalyst, and supported the same NOx occlusion reduction type catalyst as the above on the front face of the fiber layer of the downstream is applied.
[0021] By these configurations, an oxidation catalyst into the upstream part of a filter moreover, by making the downstream support an NOx occlusion reduction type catalyst, respectively Since oxidize the sulfur oxide (SOx) in exhaust gas by the oxidation catalyst of the upstream, and it is made to combine with calcium, Zn, Fe, etc. in exhaust gas, is made solid sulfate and uptake is carried out to a filter The attainment to the NOx occlusion reduction type catalyst of SOx can be prevented, and sulfur poisoning of an NOx occlusion reduction type catalyst can be avoided.
[0022] And although NOx occlusion capacity will decline if CO exists in exhaust gas when an air-fuel ratio is Lean's NOx occlusion operation since the NOx occlusion reduction type catalyst has the property which emits a nitrogen dioxide (NO2) from an NOx occulded substance, if a carbon monoxide (CO) exists In the exhaust gas purge of this invention, since it oxidizes and CO in exhaust gas is removed by the oxidation catalyst of the upstream, an air-fuel ratio can maintain highly the NOx occlusion capacity at the time of Lean.
[0023] Moreover, since a lot of CO occurs in order that there may be no oxygen (O2) into exhaust gas when it is playback operation with a rich air-fuel ratio, this CO is NO2 from an NOx occulded substance. It is NO2 emitted since this CO became a reducing agent while promoting emission. Reduction purification is efficiently carried out by the oxidation catalyst of an NOx occlusion reduction type catalyst.
[0024]
[Embodiment of the Invention] Hereafter, the exhaust gas purge of the gestalt of operation concerning this invention is explained, referring to a drawing.
[0025] The configuration of the exhaust gas purge 1 of the gestalt of this 1st operation is shown in drawing 1 .
[0026] As shown in drawing 1 , this exhaust gas purge 1 is equipment formed in the flueway 3 of a diesel power plant 2, is equipped with the filter 4 of the Wall flow type which purifies the particulate matter (PM) and nitrogen oxides (NOx) in exhaust gas G, and is constituted.





[0027] As shown in drawing 2 , this Wall flow type of filter 4 has the channel (cel) 35 of many polygon configurations used as the path of exhaust gas G in the support 30 of the structure material formed by cordierite, silicon carbide (SiC), stainless steel, etc., and is formed by the monolith honeycomb which ******(ed) the porous inlet port and porous outlet of a channel 35 of a ceramic by turns. [ of a honeycomb ]
[0028] And as shown in drawing 3 and drawing 4 , while forming the oxidation catalyst layer 20 which supported the oxidation catalyst 21 and in which aeration is possible in upstream partial 30u of the porosity wall surface 30 of this filter 4, the NOx purification catalyst bed 40 which supported the nitrogen-oxides occlusion reduction type catalyst (NOx occlusion reduction type catalyst) 41 which contains nitrogen-oxides occulded substance (NOx occulded substance) 41a and oxidation catalyst 41b in 30d of downstream parts of the porosity wall surface 30 of a filter 4 and in which aeration is possible is formed.
[0029] This oxidation catalyst layer 20 supports ****** 21, such as platinum (Pt) etc. and cerium oxide (CeO2), in porous catalyst coat layers applied to upstream partial 30u of the porosity wall surface 30 of this filter 4, such as a zeolite and an alumina (aluminum 2O3), and is formed in them possible [ aeration ].
[0030] Moreover, the NOx purification catalyst bed 40 supports the NOx occlusion reduction type catalyst 41 which becomes porous catalyst coat layers applied to 30d of downstream parts of the porosity wall surface 30 of a filter 2, such as a zeolite and an alumina, from NOx occulded substance 41a and oxidation catalyst 41b, and is formed.
[0031] The potassium in which this NOx occulded substance 41a has an NOx occlusion function (K), Alkali metal, such as barium (Ba), sodium (Na), a lithium (Li), and caesium (Cs), It is formed in one or some combination in rare earth, such as alkaline earths, such as calcium (calcium), a lanthanum (La), and an yttrium (Y), etc., and oxidation catalyst 41b is formed with catalytic activity metals, such as platinum (Pt) and a rhodium (Rh).
[0032] By this configuration, the NOx occlusion reduction type catalyst 41 As typically shown in drawing 9 , when the air-fuel ratio in exhaust gas is in the Lean condition (O2 concentration is comparatively high), occlusion of NOx is carried out by NOx occulded substance 41b. When an air-fuel ratio is in a rich condition (O2 concentration is almost zero), NOx will be emitted by NOx occulded substance 41b, and it will have the function which returns with reducing agents, such as CO and HC, by the catalysis of oxidation catalyst 41b, and purifies this emitted NOx.
[0033] Next, exhaust gas purge 1A of the gestalt of the 2nd operation is explained.
[0034] The types of the filter with which exhaust gas purge 1A of the gestalt of this 2nd operation purifies the exhaust gas purge 1 of the gestalt of the 1st operation and the particulate matter in exhaust gas (PM) as shown in drawing 5 - drawing 7 differ.
[0035] The filters 4A, 4B, and 4C of the gestalt of this 2nd operation As shown in drawing 5 - drawing 10 , it is formed with a fiber laminating type filter. Or several layers are formed in piles. the fiber layers 5a-5d of the nonwoven fabric which carried out the laminating of the fiber metallurgy group fiber of ceramics, such as an alumina, at random -- one layer -- The these fiber layers [ 5a-5d ] layered products 5A, 5B, and 5C are pinched at the heat-resistant wire gauzes 6 and 7, and it bends in the shape of bellows, and constitutes in a bell shape, and end side 4a of this hollow cylinder is blockaded. From the outside of the these bell shape fiber layers [ 5a-5d ] layered products 5A, 5B, and 5C, exhaust gas G circulates to the inside, is purified inside, and is discharged from other end side of centrum 4b 4c outside.
[0036] And as shown in drawing 8 and drawing 9 , the porous catalyst coat layer 40 which applied to the front face of fiber layer 5a of the upstream of these filters 4A and 4B the porous catalyst coat layer 20 which supported the oxidation catalyst 21, and supported the NOx occlusion reduction type catalyst 41 on the front face of 5d of fiber layers of the downstream is applied. Drawing 8 shows the example of layered product 5A which formed the porous catalyst coat layers 20 and 40 in the heat-resistant wire gauze [ of fiber layer 5a ] 6, and wire gauze 7 side of 5d of fiber layers, and drawing 9 shows the example of layered product 5B which formed the porous catalyst coat layers 20 and 40 between fiber layer 5a and fiber layer 5b and between 5d of fiber layers, and fiber layer 5c.
[0037] Or after carrying out the dipping of the fiber layers 5a and 5d of the upstream or the

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downstream to the solution of each catalyst 31 and 41 and making the fiber front face which dries and heat-treats and forms the fiber layers 5a and 5d support each catalyst 31 and 41 As shown in drawing 10 , a laminating is carried out to fiber layer 5a' which supported these catalysts 31 and 41, and the fiber layers 5b and 5c which are not supporting the catalyst for 5d', and layered product 5C is formed. in addition, the fiber layer 5 which constitutes filter 4C — the filter layer which all boils a-5d, is made to support one of catalysts, and is not supporting the catalyst may be excluded and formed.

[0038] Since according to the exhaust gas purges 1 and 1A of the above configuration it is discharged after exhaust gas G contacts an oxidation catalyst 21, passes Filters 4, 4A-4C to other backward one and contacts it further at the NOx occlusion reduction type catalyst 41, it is efficiently purified in the following processes.

[0039] First, it is O2 in exhaust gas like usual operations, such as a usual diesel power plant, a usual lean combustion gasoline engine, etc. The air-fuel ratio contained in the condition that Lean's oxygen density is comparatively high As shown in drawing 11 , by oxidation catalyst 41b of the oxidation catalyst 21 of the upstream of Filters 4, 4A-4C, or the NOx occlusion reduction type catalyst of the downstream NO in exhaust gas G O2 in this exhaust gas G It oxidizes and is NO2. It becomes and is this NO2. Since NOx occulded substance 41a, such as barium (Ba), carries out occlusion in the form of a nitrate (for example, Ba2 (NO3)) etc., NOx in exhaust gas G is purified.

[0040] Moreover, by the oxidation catalyst 21 of the upstream, oxidation purification of HC in exhaust gas G and CO is carried out, and degradation of the NOx occlusion capacity by CO of the NOx occlusion reduction type catalyst 41 is prevented. Moreover, uptake of the PM, such as SOOT (soot: soot), is carried out by the layered products 5A-5C of the porosity wall surface 30 of Filters 4, 4A-4C, or fiber.

[0041] If this condition continues, however, NOx occulded substance 41a with an NOx occlusion function Since it changes to a nitrate etc. altogether and an NOx occlusion function is lost, engine operational status is changed. The rich combustion which is an air-fuel ratio near theoretical air fuel ratio and theoretical air fuel ratio A short time O2 in exhaust gas which performs for (for example, about 0.1 seconds - about 5 seconds), and is called rich spike gas The hot exhaust gas made into abbreviation zero is generated, and it sends and regenerates for the NOx occlusion reduction type catalyst 41.

[0042] Most oxygen densities with the rich air-fuel ratio which reproduces the NOx occlusion reduction type catalyst 41 and in a zero state At the upstream of Filters 4, 4A-4C, it is O2. Since there is almost nothing, HC and CO pass to the downstream, without oxidizing, and at the downstream, it is O2. Since there is almost nothing The nitrate (barium nitrate) of NOx occulded substance 41a which carried out occlusion of NOx as shown in drawing 12 etc. is return and NO2 which was carrying out occlusion to the original condition (barium). It emits.

[0043] Since there is much CO at the time of this playback, it is NO2 from NOx occulded substance 41a. Since emission and reduction purification can be promoted, the time amount which playback of NOx occlusion capacity takes can be shortened.

[0044] this emitted NO2 the inside of exhaust gas -- O2 CO, HC, and H2 in the exhaust gas which has passed the layered products 5A-5C of the porosity wall surface 30 or fiber by the catalysis of oxidation catalyst 41b since it does not exist etc. -- a reducing agent -- carrying out -- nitrogen N2 it is returned and purifies -- having -- H2 O and CO2 It is discharged. Moreover, uptake of the PM, such as SOOT, is carried out by the layered products 5A-5C of the porosity wall surface 30 or fiber.

[0045] And since it oxidizes by the oxidation catalyst 31 of the upstream, and the sulfur oxide (SOx) in exhaust gas is combined with calcium, Zn, Fe, etc. in exhaust gas, and can be made into solid sulfate and this sulfate can carry out uptake of it in the layered products 5A-5C of the porosity wall surface 30 or fiber, the contact to the NOx occlusion reduction type catalyst 41 of SOx is prevented, and sulfur poisoning of the NOx occlusion reduction type catalyst 41 can be avoided.

[0046]

[Effect of the Invention] According to the exhaust gas purge of this invention, the following





effectiveness can be done so as explained above.

[0047] Without always supplying the reducing agent for NOx reduction, with the filter which supported the oxidation catalyst and the NOx occlusion reduction type catalyst, by uptake, the occlusion according NOx to an NOx occlusion reduction type catalyst, and the emission and reduction in exhaust gas, while being able to oxidize and purify, since PM in exhaust gas can be purified efficiently, a reducing-agent feeder becomes unnecessary about it, and aggravation of fuel consumption can be prevented.

[0048] An oxidation catalyst into the upstream part of a filter and by moreover, the configuration which arranges an NOx occlusion reduction type catalyst in a downstream part Since oxidize the sulfur oxide (SOx) in exhaust gas by the oxidation catalyst of an upstream part, it is made to combine with calcium, Zn, Fe, etc. in exhaust gas, it considers as the sulfate of the solid-state which can carry out uptake with a filter and uptake is carried out with a filter SOx in exhaust gas can prevent reaching to an NOx occlusion reduction type catalyst, and can avoid sulfur poisoning of an NOx occlusion reduction type catalyst.

[0049] Furthermore, since an air-fuel ratio carries out oxidation removal of CO in exhaust gas by the oxidation catalyst of the upstream of a filter in Lean's NOx occlusion operation Degradation of the NOx occlusion capacity by CO is prevented, and the high rate of purification can be maintained, and it sets to playback operation with a rich air-fuel ratio, and is O2 in exhaust gas. By CO generated in order for there to be nothing NO2 from an NOx occulded substance Emission and reduction purification can be promoted and the time amount which playback of NOx occlusion capacity takes can be shortened.

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## DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing arrangement of the exhaust gas purge concerning this invention.
[Drawing 2] It is drawing concerning this invention showing the configuration of the 1st Wall flow type filter of the exhaust gas purge of the gestalt of operation.
[Drawing 3] It is the enlarged drawing of the filter of drawing 2 .
[Drawing 4] It is the partial enlarged drawing of the filter of drawing 2 .
[Drawing 5] It is drawing concerning this invention showing the configuration of the 2nd fiber laminating type filter of the exhaust gas purge of the gestalt of operation.
[Drawing 6] It is drawing showing the flow of the exhaust gas in the filter of drawing 5 .
[Drawing 7] It is the partial enlarged drawing of drawing 6 .
[Drawing 8] It is drawing showing the 1st example of the laminated structure of the filter of drawing 5 .
[Drawing 9] It is drawing showing the 2nd example of the laminated structure of the filter of drawing 5 .
[Drawing 10] It is drawing showing the 3rd example of the laminated structure of the filter of drawing 5 .
[Drawing 11] Typical drawing showing the mechanism of the NOx purification by the NOx occlusion reduction type catalyst shows the condition that air-fuel ratios, such as combustion, usually supply the exhaust gas of the Lean condition.
[Drawing 12] Typical drawing showing the mechanism of the NOx exhaust air purification by the NOx occlusion reduction type catalyst shows the condition that the air-fuel ratio supplies the exhaust gas of a rich condition.
[Description of Notations]
1, 1A, 1B, 1C Exhaust gas purge
2 Engine
3 Flueway
4 Wall Flow Type Filter
4A, 4B, 4C Fiber laminating type filter
4s The fiber layer of the upstream
4d Fiber layer of the downstream
20 Oxidation Catalyst Layer (Porous Catalyst Coat Layer)
21 Oxidation Catalyst
30 Porosity Wall Surface
40 Nitrogen-Oxides Purification Catalyst Bed (Porous Catalyst Coat Layer)
41 Nitrogen-Oxides Occlusion Reduction Type Catalyst (NOx Occlusion Reduction Type Catalyst)
41a Nitrogen-oxides occulded substance (NOx occulded substance)
41b Oxidation catalyst
G Exhaust gas





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